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Alternative Thermochemical Cycle Evaluation

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Overview

Time Line

- Start date: 10/04
- End date: 09/07
- % complete: 90%

Barriers

- Unknown thermodynamic data
- Unknown chemistry
- Short timeline

Budget

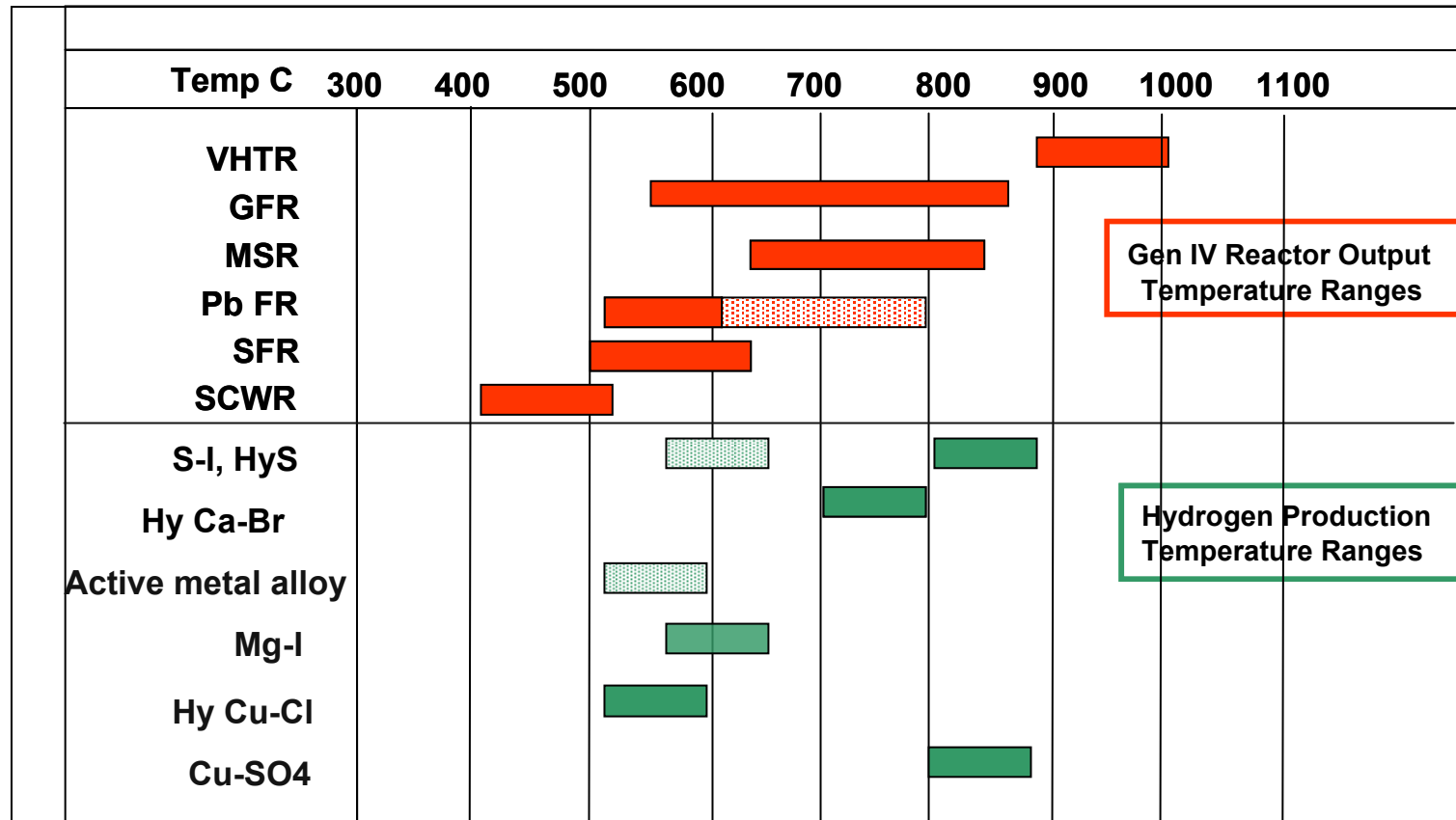
- FY 06 = \$1,043K
- Funds supported 8 universities
- Complementary program supported by DOE-EERE

Partners

- Eight universities
- Information exchange
 - Atomic Energy of Canada, Ltd.
 - Commissariat à l'Energie Atomique
 - Ontario Institute of Technology

Objective: Balance temperature portfolio of nuclear heating sources with thermochemical cycles for H₂ generation

- Electrical generation - **Gen IV Energy Conversion Program**
- Hydrogen production - **Nuclear Hydrogen Initiative (NHI)**



Approach

- **Identify promising cycles from the literature with various maximum temperatures to match heat output from different nuclear reactors**
- **Invite university participation to evaluate cycles using consistent methodology**
 - Clemson, Howard, MIT, Pennsylvania State University, Rensselaer Polytechnic Institute, Tulane, University of South Carolina, University of Illinois-Chicago (UIC)
 - NHI methodology consists of 3 levels of evaluation
 - *Level 1 based on stoichiometric reactions*
 - *Level 2 based on equilibrium considerations*
 - *Level 3 based on 'real' chemistry to the extent it is known*
 - *Pinch analysis used for heat management in all levels*
- **Determine critical R&D needs or recommend no further work**
- **Down select 1 or 2 of the most promising cycles for further R&D**

What is a promising alternative thermochemical cycle?

■ Chemically viable

- Determined from literature or current experimental work
- No important competing reactions
- Fast kinetics and high yields

■ Thermodynamically feasible

- Free energies for all reactions are within ± 15 kcal or about 60 kJ
- Determined from thermodynamic databases

■ Thermally efficient

- Literature results used for initial assessment of promise
- Recalculated values from NHI methodology by the universities used for final assessment

■ R&D needs compatible with DOE timeline

■ Cost competitive with gasoline equivalent

- To be determined
 - Currently \$2.00-3.00/gge (*delivered, untaxed, 2005\$, by 2015*),
independent of the pathway used to produce and deliver hydrogen

Efficiency results from university evaluations

	Efficiency % (LHV)		
Cycle	Level 1	Level 2	Level 3
Active metal alloy	30-48	Insufficient data	
Ca-Br	46	In progress	Insufficient data
Ce-Cl	Not calculated	16.8	20.9 ^a
Cu-Cl	42-50	38-48	43
Cu-SO ₄	47.1	25-40	52.4
Fe-Cl	29	18.5	NA
Hybrid Cl ₂	34.3	32.1	34-35
Mg-I	47	45	46 ^{a,b}
V-Cl	52.5	48.9	46

^a Level 3 calculated for H₂ final pressure of 1 bar

^b Thermodynamic data in question; preliminary estimate

Other positive attributes for these cycles

Cycle	Advantages
Active Metal Alloy (Hybrid)	Simple unit operations, minimal separations
Ca-Br (Hybrid)	Maximum temperature $\sim 750^{\circ}\text{C}$, leverage R&D from UT-3 cycle and Ispra cycles
Cu-Cl (Hybrid)	Maximum temperature $\sim 550^{\circ}\text{C}$; completed proof-of-concept work
Cu-SO₄	High projected efficiencies if electrochemical rxn. can be converted to a thermal one; less aggressive chemicals than in other sulfur cycles; leverage R&D from S-I cycle
Hybrid Cl₂	Relatively simple, two unit operations
Mg-I	Maximum temperature $\sim 600^{\circ}\text{C}$; leverage R&D from S-I cycle to handle HI
V-Cl	High projected efficiencies; on hold pending results of reverse Deacon reaction study in the hybrid chlorine cycle

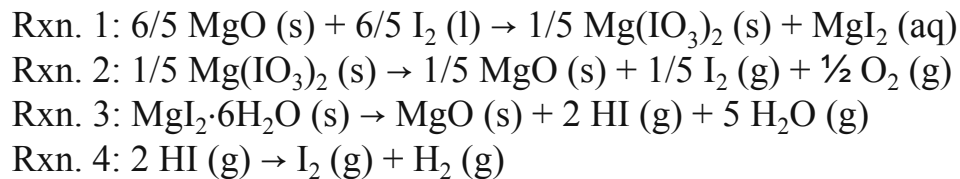
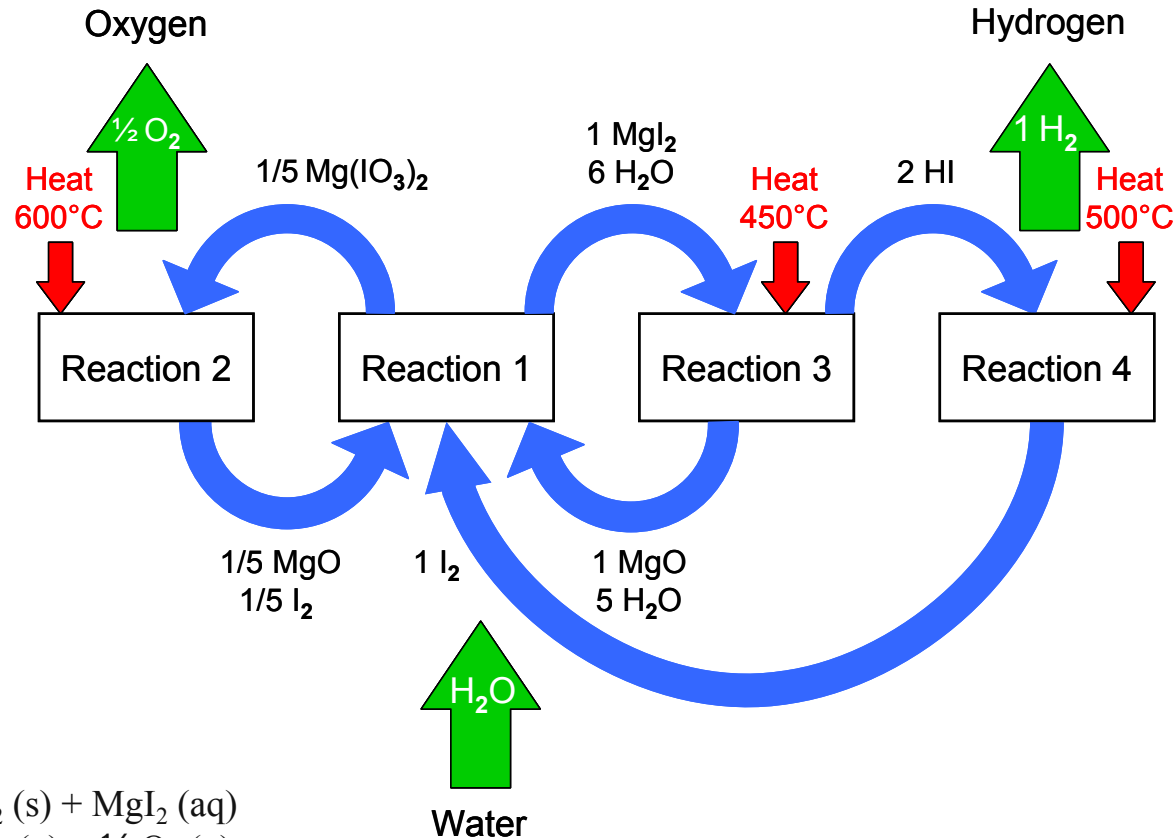
Challenges for further development of these cycles

Cycle	Challenges
Active metal alloy	No proof of concept work, unknown chemistry, absence of thermodynamic data for most species
Ca-Br	No proof of concept work for bromination reaction, missing thermodynamic data
Cu-Cl	Development of the electrochemical reaction and optimization of conditions for hydrolysis reaction
Cu-SO ₄	High temperature for CuSO ₄ decomposition, conversion of electrochemical reaction to thermal one
Hybrid Cl ₂	High electrical input for electrolysis of HCl, challenging separations and temperatures in reverse Deacon reaction (RDR)
Mg-I	HI-I ₂ or HI _x decomposition, excess water handling, azeotrope formation
V-Cl	Separations/high temperature of the reverse Deacon reaction, kinetics of the chlorination reaction

Mg-I: $T_{max} = 600^{\circ}\text{C}$

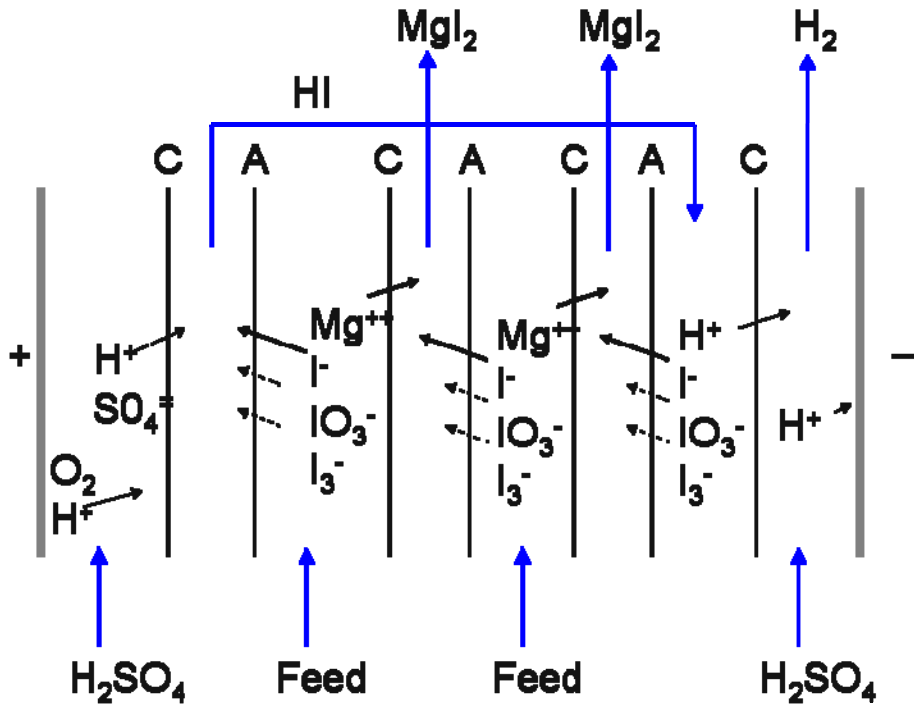
■ Mg-I cycle was extensively studied in Japan

- Yields and reaction kinetics are sufficient
- Most separations relatively easy
- Most challenging aspect is HI decomposition
 - *Leverage R&D from S-I cycle*
- Excess water and iodine required



Mg-I: $T_{max} = 600^{\circ}\text{C}$, Cont.

- Use electrodialysis to remove dissolved iodate in the MgI_2 solution
- Electrodialysis costs are relatively low



Method	Energy (kWh/ton water)
Distillation	620
Multiple Effect	100
Reverse osmosis	7
Electrodialysis	3 to 8, low salt 15 to 25, high salt

Hybrid chlorine: $T_{\max} \leq 850^{\circ}\text{C}$

R&D Emphasis on the reverse Deacon reaction (RDR)

■ Two reaction cycle

- RDR: $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ 850°C
- $2\text{HCl}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$ (electrolytic) 75°C
 - *A small scale unit for electrolyzing HCl (g) is available*

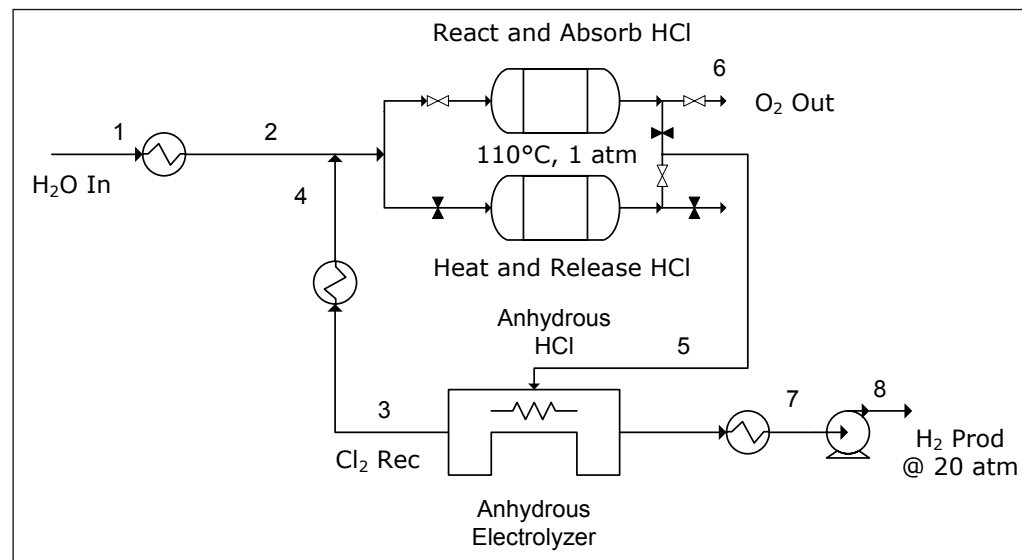
■ Challenge lies in the RDR

- 60% yield at 850°C

■ Increase yield by removing HCl or O_2

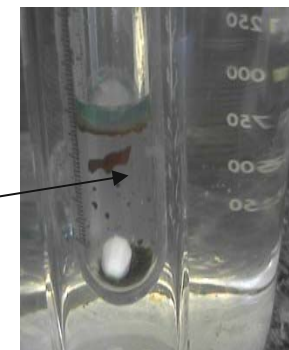
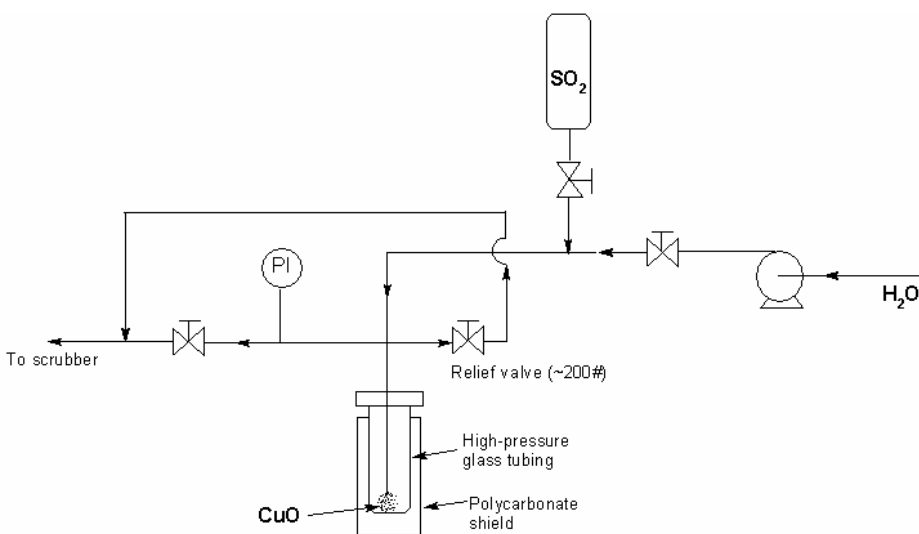
■ Clemson studied acidic sorbers

- Zeolite gave best results
 - *O_2 product observed*
 - *Proof-of-concept !!*



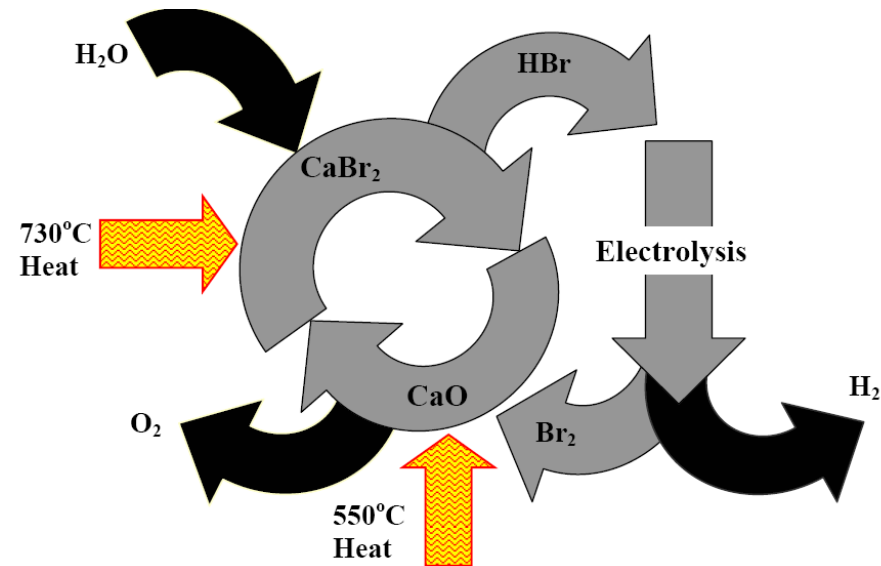
Hybrid (?) CuSO_4 : $T_{\text{max}} \leq 850^\circ\text{C}$

- Tulane's concept was to convert hydrogen generation reaction from a proven electrochemical one to a thermal one by using liquid SO_2 instead of gaseous SO_2
 - Large increase in efficiency if successful but Chevrel's salt formed
 - Decrease temperature of CuSO_4 decomposition by leveraging R&D in the S cycles
 - CuSO_4 is less aggressive than H_2SO_4
- $\text{CuO} + \text{H}_2\text{O} + \text{SO}_2 \rightleftharpoons \text{CuSO}_4 + \text{H}_2(\text{g}) \quad 25^\circ\text{C}$
- $\text{CuSO}_4 \rightleftharpoons \text{CuO}(\text{g}) + \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \quad 850^\circ\text{C}$



New ideas in the hybrid Ca-Br cycle: $T_{\max} = 750^{\circ}\text{C}$

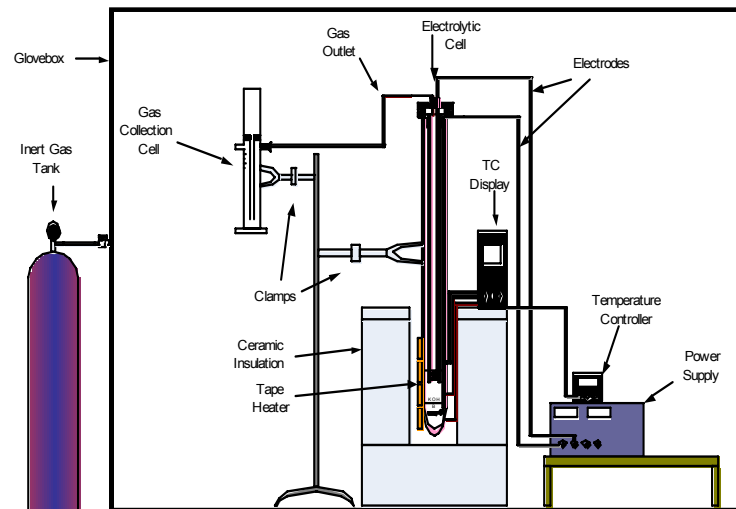
- UIC calculated Level 1 efficiency of 46% (LHV) and developed reactor sparging model
- Sparging of steam through molten CaBr_2 successfully demonstrated at Argonne
 - High yields of HBr in the hydrolysis reaction
 - H_2O droplets sparged into CaBr_2 melt
 - CaO dissolved in melt and complex formed
- HBr dissociation using PEM electrolyzer cell looks promising
- Experiments to regenerate melt by sparging Br_2 into CaO-CaBr_2 melt planned



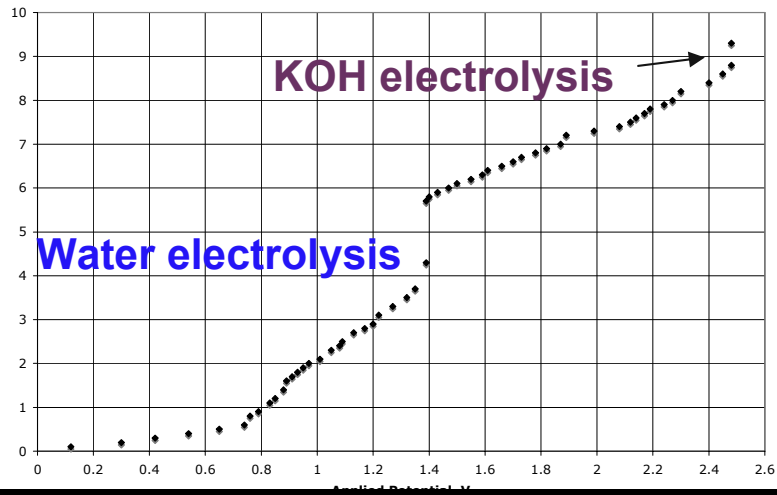
Hybrid active metal alloy cycle: $T_{\max} = 575^{\circ}\text{C}$

Two reactions:

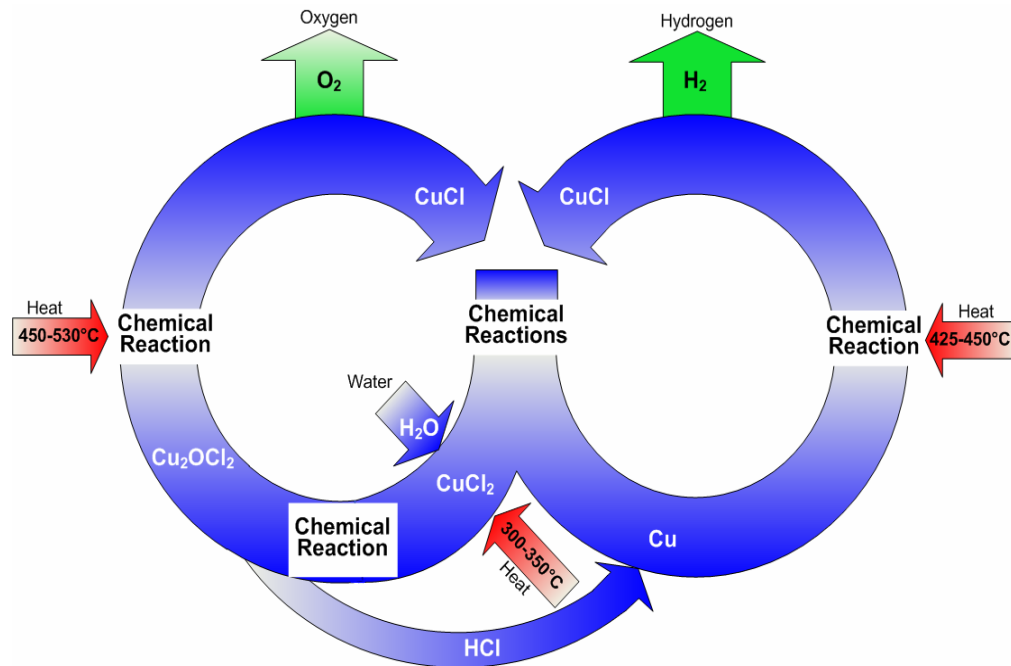
- $\text{KBi} + \text{H}_2\text{O} \leftrightarrow \frac{1}{2} \text{H}_2 + \text{KOH(l)} + \text{Bi}$
- $\text{KOH(l)} + \text{Bi(l)} \leftrightarrow \frac{1}{4} \text{O}_2(\text{g}) + \frac{1}{2} \text{H}_2(\text{g}) + \text{KBi(l)}$
 - Cathode: $\text{K}^+ + \text{Bi(l)} + e^- \leftrightarrow \text{KBi(l)}$
 - Anode: $\text{OH}^- \leftrightarrow \frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) + e^-$
 - $\text{OH}^- \leftrightarrow \frac{1}{2} \text{H}_2\text{O(g)} + \frac{1}{4} \text{O}_2(\text{g}) + e^-$
 - Anode reaction not known yet



Polarization Curve



Hybrid Cu-Cl cycle: $T_{max} = 550\text{ }^{\circ}\text{C}$



■ Proof of principle experiments completed for all reactions

- $2\text{Cu} + 2\text{HCl} \leftrightarrow 2\text{CuCl} + \text{H}_2$
- $4\text{CuCl} \leftrightarrow 2\text{CuCl}_2 + 2\text{Cu}$
- $\text{CuCl}_2 + \text{H}_2\text{O} \leftrightarrow \text{Cu}_2\text{OCl}_2 + 2\text{HCl}$
- $\text{Cu}_2\text{OCl}_2 \leftrightarrow 2\text{CuCl} + \frac{1}{2}\text{O}_2$

■ Reaction yields and kinetics indicate no showstoppers

■ Hydrolysis reaction being studied to minimize competing reaction

- $2\text{CuCl}_2 \leftrightarrow 2\text{CuCl} + \text{Cl}_2$

■ Study of electrochemical reactions to minimize capital costs and maximize overall cycle efficiency

- $2\text{CuCl} + 2\text{HCl} \leftrightarrow \text{H}_2 + \text{CuCl}_2$ or
- $2\text{Cu} + 2\text{HCl} \leftrightarrow 2\text{CuCl} + \text{H}_2$

Summary of current evaluation results for alternative thermochemical cycles

- **All proof of principle work completed for Cu-Cl and Mg-I cycles**
 - Optimization work now ongoing
 - *Hydrolysis reaction and electrochemical cell development for Cu-Cl cycle*
 - *HI_x decomposition (in R&D for S-I) and separations for Mg-I*
- **Proof of principle experiments almost complete for Ca-Br and hybrid Cl₂ cycles**
 - Two reactions demonstrated; oxidation of CaBr₂ to CaO via regeneration of bed in progress
 - Qualitative evidence for O₂ formation in the reverse Deacon reaction (RDR)
- **Possible show stoppers**
 - Experiments indicated formation of Chevreul's salt in the Cu-SO₄ study
 - Experiments showed no hydrogen formation in the active metal alloy cycle
- **V-Cl cycle on hold pending results of the RDR study but unlikely to meet DOE timeline**

Future work

■ Down select one or two of the most promising cycles in June 2007 using the following metrics:

- Efficiency evaluations and results of ongoing experimental work
- Assessment of critical needs for further development with respect to the DOE timeline and available technology
 - *Any potential showstoppers?*
- Availability of heat sources
 - *For VHTR, GFR, MSR: All cycles*
 - Assumes current maximum temperatures for Cu-SO₄ and hybrid Cl₂ are lowered, which seems possible at this time
 - Use excess heat for electricity production for lower temperature cycles
 - *For Pb FR, SFR, and SCWR*: Mg-I, hybrid Cu-Cl, hybrid active metal alloy if ongoing R&D is successful*

**Assumes that it is possible to adapt pressure tube technology to obtain higher maximum temperatures for the SCWR*

Project summary

- **Relevance:** Needed to balance the thermochemical cycle portfolio with various heat sources
- **Approach:** Identify promising cycles from the literature and engage universities to reevaluate them using the Nuclear Hydrogen Initiative (NHI) consistent methodology and to start experimental work for critical R&D
- **Technical Accomplishments and Progress:** Eight cycles evaluated and six chosen for further R&D. Experimental work in progress. Down selection to 1 or 2 cycles in June 2007
- **Technology Transfer/Collaborations:** Active partnership with Atomic Energy of Canada, Ltd., University of Ontario Institute of Technology, and Commissariat à l'Energie Atomique, University of Nevada-Las Vegas, Sandia National Laboratory, and the universities involved in the program
- **Proposed Future Research:** Continue R&D for the most promising one or two alternative cycles
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